

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 0 655 073 B1**

(12)

**EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:

**30.12.1998 Bulletin 1998/53**

(51) Int Cl.<sup>6</sup>: **C08F 4/02**

(86) International application number:  
**PCT/FI92/00170**

(21) Application number: **92917458.9**

(87) International publication number:  
**WO 92/21705 (10.12.1992 Gazette 1992/31)**

(22) Date of filing: **29.05.1992**

**(54) METHOD FOR PREPARING SOLID CARRIER PARTICLES OF EQUAL SIZE FOR  
POLYMERIZATION CATALYST USING ROTATING ATOMIZING MEANS**

**VERFAHREN ZUR HERSTELLUNG FESTER TRÄGERTEILCHEN GLEICHER GRÖSSE FÜR  
POLYMERISATIONSKATALYSATOREN MIT HILFE ROTIERENDER  
PULVERISIERUNGSEINRICHTUNGEN**

**PROCEDE DE PREPARATION DE PARTICULES PORTEUSES SOLIDES D'EGALE GROSSEUR  
POUR UN CATALYSEUR DE POLYMERISATION, ET CONSISTANT A UTILISER DES ELEMENTS  
DE PULVERISATION ROTATIFS**

(84) Designated Contracting States:  
**BE DE FR GB IT**

(30) Priority: **31.05.1991 FI 912639**

(43) Date of publication of application:  
**31.05.1995 Bulletin 1995/22**

(73) Proprietor: **BOREALIS A/S**  
**2800 Lyngby (DK)**

(72) Inventors:  
• **KOSKINEN, Jukka**  
**SF-02160 Espoo (FI)**

• **LOUHELAINEN, Jarmo**  
**SF-00960 Helsinki (FI)**

(74) Representative: **Burrows, Anthony Gregory**  
**Business Centre West**  
**Avenue One, Business Park**  
**Letchworth Garden City**  
**Hertfordshire SG6 2HB (GB)**

(56) References cited:  
**EP-A- 20 818** **WO-A-87/07620**  
**US-A- 4 303 200**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

**EP 0 655 073 B1**

## Description

The invention relates to a method for the preparation of solid carrier particles for a polymerization catalyst, in which there is provided a melt of a complex composition having the formula (I)



in which ROH depicts an aliphatic alcohol, R is a  $\text{C}_1$ - $\text{C}_6$  alkyl, ED depicts an electron donor, n is 1 to 6 and m is 0 to 1; the melt provided is fed to a nozzle; the melt is sprayed from the nozzle to a spraying area in which it is divided into fine melt droplets and solidifies to solid carrier particles; and the solid carrier particles are recovered. The invention also relates to a method in which the olefin polymerization catalyst is provided by bringing the recovered solid carrier particles together with a transition metal compound being catalytically capable of activation, such as titanium tetrachloride, and the use of the olefin polymerization catalyst thus prepared together with a cocatalyst and alternately an external electron donor for the polymerization of olefins.

Polymerization catalysts and particularly catalysts of Ziegler-Natta type nowadays typically comprise an inert solid carrier, on which the actual active catalyst component or the mixture or complex formed by the catalytical compounds is layered. The chemical composition of the particles, the structure of the surface, the morphology, the particle size and the particle size distribution of such a carrier are of major significance for the activity of the catalyst and the properties of the polymer to be obtained. With a very active catalyst, namely, polymer can be produced from which thanks to its purity no catalyst residues need to be removed. The surface structure and the morphology of the carrier, on the other hand, affect on the morphology of the polymerization product itself, for it has been noticed that the morphology of the catalyst is repeated in the structure of the polymer (the so-called replica phenomenon). When the aim is a flowing product polymer having the desired morphology and a narrow particle size distribution, which is desirable in view of the objects of use of many of the processing processes, the properties of the carrier should, because of the replica phenomenon, be made corresponding.

The catalysts of the above-mentioned type are nowadays often formed of magnesium based carrier substance, which has been treated with a transition metal compound like titanium halide and often also with an electron donor compound. It is also known that a carrier can be brought into a preferred chemical composition having a certain surface structure, a certain morphology, a certain particle size and a certain particle size distribution by letting it crystallize as a complex of one of its crystal solvents.

In the method according to EP publication 65,700 and US 4,421,674 the titanium halide is brought to react with a magnesium chloride catalyst carrier being in the form of micro balls, after which the reaction product particles are recovered by physical means and are mixed together with an organometallic compound. In the method the carrier is prepared by providing a solution, which essentially contains magnesium dichloride dissolved in ethanol and a spray-drying of the solution is carried out by spraying it into a flow of nitrogen gas, the inlet and outlet temperatures of which are high. As a result magnesium dichloride particles of very even size having the form of a ball are obtained. In this method the high temperature evaporates, however, a great deal of the crystal solvent, whereby porosity is created on the surface of the carrier and its activation capability decreases. This leads to a solid catalyst having a satisfactory particle size distribution, but the activity and mechanical strength of the catalyst is poor due to the porosity.

In the FI-patent application 862469 (Neste Oy) there is disclosed a method for the preparation of a carrier, in which there does not appear any porosity decreasing the activity and the mechanical strength.

In the method the carrier complex formed by the carrier and the crystal solvent is melt to a clear liquid. When the liquid is conducted through the nozzle and the spraying space into the crystallizing space cooled with cold nitrogen gas the carrier complex crystallizes to small particles having a spherical form which are very flowing and loose. Furthermore, the carrier complex crystallizes without considerable evaporation of the crystal solvent. Hereby a nacreous non-porous surface is obtained, which is particularly well suitable for the preparation of an active catalyst. When such a preactivated carrier is brought into contact with a titanium compound, abundantly of catalytically active complexes between the  $\text{MgCl}_2$  and the titanium compound, are formed onto the surface of the carrier, when the crystal solvent leaves.

The above-mentioned Finnish method has in result easily activating carrier compounds and complexes. A drawback of this so-called spray-crystallizing method is, however, that the droplets formed are not of fully equal size and that they are partly agglomerated. Although, as to their surface structure, more useful carrier particles are obtained by this method than e.g. by spray-drying, the problem thus is that an unsatisfactory particle size distribution is formed and that the particles are partly agglomerated.

The aim of the present invention is to provide such solid carrier particles of the polymerizing catalyst that are both active and in suitable form, loose from each other and of equal size. Hereby, the aim is to prepare new carrier particles

having chemical structure, surface structure, morphology, size, and size distribution as advantageous as possible in view of the activity of the catalyst and the form, size and size distribution of the particles of the polymer to be obtained. These aims have now been reached by the improvement of the above-mentioned spray-crystallizing method, for which is mainly characterizing that the melt used in the method is sprayed through a nozzle that rotates or attached to which is a member that rotates and launches melt outwards from the rotating center to the spraying area. It has thus been realized that the preferred surface structure of the carrier particles obtained by spray-crystallization can be combined with the narrow particle size distribution by using a rotating nozzle or a corresponding device.

The method according to the invention begins with the stage in which a melt of the complex compound is obtained. It can take place by reacting the components of the complex compound with each other at so high a temperature that they react with each other and remain in the reaction vessel in the form of a melt complex, or so that the ready complex is melted for the use according to the present method.

As has been mentioned above, the main component of the carrier particles obtained by the method according to the invention is magnesium chloride. It must be either fully non-aqueous or then its water content shall be very low and it preferably shall contain 1% by weight of water at the most.

The other component of the complex compound is alcohol. It usually is an aliphatic alcohol, the alkyl group of which contains 1 to 6 carbon atoms. Preferred aliphatic alcohols are methanol and/or ethanol and the most preferable is ethanol. The alcohol used in the preparation of the complex compound must be dry and preferably it shall contain about 2% by weight of water at the most.

The third and optional component of the complex compound used in the invention is a donor compound. When selecting donor compounds the criterion is that they improve the polymerization and the drop-formation of the melt without disturbing the melting and spray-crystallization of the complex compound containing these donor compounds.

The electron donor can thus be an aliphatic or aromatic carboxylic acid, an aliphatic or aromatic alkyl ester of the carboxylic acid, an ether, an aliphatic or aromatic ketone, an aliphatic or aromatic aldehyde, an aliphatic or aromatic alcohol, an aliphatic or aromatic halide, such as acid halide, an aliphatic or aromatic nitrile, an aliphatic or aromatic amine, an aliphatic or aromatic fosfine, or an aliphatic or aromatic silicon ether. Preferred electron donors are the aromatic dicarboxylic acids, such as dialkyl phthalates, particularly di-isobutyl phthalate and the aliphatic dicarboxylic acids, such as dialkyl maleates, particularly diethyl maleate.

The preparation of the melt of the complex compound used in the method takes place so that the magnesium chloride, alcohol and possibly internal donor of the catalyst are mixed together. The portion of the magnesium chloride is hereby preferably within the range 30 to 55% by weight, the portion of alcohol preferably within the range of 55 to 70% by weight and the portion of the internal donor is preferably within the range of 0 to 0.2 gram molecular percent. The dosing order to the reactor can be anyone; according to one embodiment to the reactor is first dosed the magnesium chloride and then the alcohol and the optional internal donor.

After that the reactor is closed and the heating is started. The temperature is preferably regulated above the melting point of the complex created, typically within the range 90 to 130°C, depending, however, on the composition of the complex melt created. At the final stage mixing and additional heating close to the upper limit of the temperature range can be used.

The agitation time of the melt depends on the amount of the magnesium chloride to be dosed e.g. so that 26kg of magnesium chloride requires an agitation for four hours at the highest temperature, e.g. in regard to magnesium chloride-ethanol complex at 130°C and 52kg of magnesium chloride an agitation of six hours at the same temperature.

As was mentioned already in the beginning of the application, for the spray-crystallization according to the invention is prepared a melt of a complex compound having the formula (I)



(I)

in which ROH depicts the above-mentioned aliphatic alcohol, R is C<sub>1</sub>-C<sub>6</sub>-alkyl, ED depicts the above-mentioned electron donor, n is a figure between 1 to 6 and m is a figure between 0 to 1, whereby m can also be 0. According to one preferred embodiment n is between 3 to 4. According to one embodiment m is of the order of magnitude about 0.05.

When the melt of the complex compound has been achieved it is fed to the nozzle. The feeding rate is hereby about 10 to 50kg/h. The feed takes place by a dosage pump and its amount and evenness are preferably achieved by means of a valveless cylinder dosage pump and a pulse attenuator. The temperature of the melt is kept constant and accurately regulated in the feed piping and the pump preferably by the aid of the oil heating mantle of the pipe. Hereby it is advantageous that the temperature of the melt is accurately regulated a little above the melting point of the melt. The temperature should be high enough so the melt would not crystallize in the feeder line and the drop formation of the melt would be efficient due to the low viscosity and the surface tension, and, on the other hand, low enough so alcohol would not evaporate away from the nozzle. According to one embodiment the feed temperature of the melt is

between 100 and 140°C. It is also advantageous if the feeding rate of the melt to the nozzle is about 10 to 50kg/h. The amount of the evaporating alcohol is below 5% by weight. Be it mentioned that in spray-drying typically more than 30% by weight of alcohol evaporates.

After this the melt of the complex compound is sprayed from the nozzle to the spraying area, where it is divided into fine melt-droplets. According to the invention the spraying takes place through a nozzle which rotates or which has a member attached to it that rotates and throws melt outwards from the rotating center to the spraying area. The fundamental idea of the invention is the spraying of a complex melt that does not easily form droplets to the spraying area by means of a rapidly rotating member.

The rotating member dividing the melt into droplets can be a separate member arranged in connection with the nozzle or the nozzle itself can be rotating.

The rotating rate of the rotating nozzle or the member being attached to it is according to one preferred embodiment 10,000 to 30,000rpm, preferably 18,000 to 25,000rpm.

To the comminution of a melt complex compound is preferably used a rotating nozzle. The nozzle is hereby preferably a hollow disc rotating around its axis, inside which the melt is led and from holes in the outer surface of the periphery of which the melt is forced out by the aid of centrifugal force. According to one embodiment the diameter of the rotating hollow disc nozzle is about 100 to 150mm. Its outer periphery surface hereby has preferably four nozzle holes, the diameter of which preferably is about 4mm. The rotating hollow disc nozzle is preferably closed in structure so that its hose through the inlet opening is in connection with the feeder pipe of the melt and through the openings mentioned is in connection with the spraying area. By this construction is prevented the pumping of the gas from the nozzle, which causes increasing evaporation of alcohol and porosity of the droplets.

From the nozzle the melt of the complex compound transfers to the spraying area around the nozzle, where it is divided into fine melt droplets. To the spraying area is preferably conducted inert gas, which is preferably conducted close to the nozzle. The temperature of the inert gas is preferably about 20 to 40°C and the flow amount is preferably about 500kg/h. The intention of the inert gas flow is to prevent the colliding of the melt droplets to each other and their agglomeration. Hereby the matter is affected, except for the temperature and the flow amount of the gas, by its flowing direction, which can be directed e.g. by means of dividing plates so that the inert gas preferably rotates in the same direction as the rotating nozzle or the rotating member being attached to it.

From the spraying area the melt of the complex compound, which can also contain solid particles, is transferred to the cooled crystallization area, where the final solidification to solid carrier particles of even size takes place. A crystallization equipment has been developed for the spray-crystallizing process concerned which enables the preparation of high-quality carrier powder. By the equipment a high bulk density of the carrier powder, a narrow particle size distribution, loose particles, and the property of being easy sieved in order to achieve an even narrower particle size distribution, are achieved. The capacity of the equipment does not cause problems and the production by it is easy and labour saving.

According to one preferred embodiment a vertical chamber is used, in the upper end of which the nozzle mentioned is situated, in the upper portion around the nozzle and a little below it there is the spraying area, in the lower portion there is the crystallizing area and in the lower end there is the recovery opening of the carrier particles. The melt of the complex compound is fed through the rotating nozzle or respective to the spraying area in the form of small droplets and droplets of even size. The melt droplets coming from the rotating nozzle or respective distribute thanks to the nitrogen gas flow fed to the upper portion of the chamber in non-agglomerated state into the spraying area. The conditions of the spraying area are regulated so that the surface temperature of the sprayed melt droplets remains within the temperature range, in which they, when they collide with each other, do not easily agglomerate and, on the other hand, the evaporation of the alcohol contained therein is as insignificant as possible. Such a temperature of the melt droplets is a little below the melting point. The temperature of the nitrogen fed to the spraying area depends on the chemical composition of the melt and it preferably is the above-mentioned 20 to 40°C.

From the spraying area, in which some kind of solidification can take place, the droplets or particles fall against the crystallization area in the lower portion of the chamber. To the crystallization area or between the crystallization area and the spraying area in the middle portion of the chamber is preferably conducted inert gas. The temperature of this inert gas preferably is between -50 to +20°C and its flow amount preferably is of the order of magnitude about 300g/h. Hereby the droplets or particles settling apart of each other from the spraying area are crystallizing efficiently and the colliding of the crystallizing particles to each other is as insignificant as possible until even the surface of the particles has crystallized and the particles cannot agglomerate any longer.

The inert gas fed both to the upper portion of the chamber and to the middle and lower portion of it preferably is dry nitrogen. It is preferable to remove the inert gas through the outlet pipe or opening situated in the lower end of the chamber.

Finally, the solid carrier particles are recovered. This takes place preferably through an outlet opening located at the lower end of the above-mentioned chamber.

The method according to the present invention for the preparation of the solid carrier particles of a polymerization

catalyst is best suited for providing such non-porous particles, the SPAN number describing the particle size distribution of which is between 1.1 to 1.6.

The recovered solid carrier particles are then brought together with a transition metal compound being able to catalytically activate, such as titanium tetrachloride, for providing an active olefin polymerization catalyst. The olefin polymerization catalyst prepared by the method can be used together with a cocatalyst and optionally together with an external electron donor for the polymerization of olefins.

In the following the invention is described more closely with reference to figures, in which

fig. 1 depicts a crystallizing equipment used in one embodiment of the method according to the invention and fig. 2 depicts a rotating type of nozzle used in one embodiment of the invention.

The crystallization equipment presented in figure 1 comprises a chamber 1 for spraying and crystallization, a reactor 2 for the preparation and/or melting of the complex and a feeding equipment 3 for the feeding of the melt complex compound from the reactor 2 to the chamber 1. The chamber comprises a nozzle 4, a spraying area 5, and a crystallization area 6. In the upper end of the chamber 1 there is the feed pipe 7 for inert gas, which leads in the middle of the chamber close to the nozzle 4. To the upper end of the chamber 1 is also arranged guide plates 8 of the inert gas flow, by which the inert gas flow is guided to minimize the agglomeration of the melt droplets. The temperature of the inert gas fed to the upper end of the chamber 1 is  $T_1$  and its flow amount is  $F_1$ .

Beneath the spraying area 5 of the chamber 1 there is another inlet pipe 8 of inert gas, from which inert gas is conducted to the middle portion of the chamber 1. The temperature of the gas fed to the middle portion is  $T_2$  and the flow amount  $F_2$ .

Beneath the inlet opening of the inlet pipe 8 for the inert gas situated in the middle portion of the chamber 1, there is in the chamber 1 a crystallization area 6. In the lower portion of the crystallization area 6 there is an outlet pipe 9 for the gas, through which all inert gas is removed.

At the lower end of the chamber 1 there is in the middle an outlet opening 10 for the finished product.

Reactor 2 is through pipe 11 in connection with the feed pump 12 of the melt, which is e.g. a valveless cylinder dosage pump. Between the pump 12 and the chamber 1 there is pipe 13, which is furnished with a pulse attenuator 14.

The piping between the reactor 2 and the chamber 1 is furnished with a heating mantle 15.

The method according to the present invention acts apparatus technically so that the components of the complex compound are fed to the reactor 2, in which they are changed by means of heat and agitation to a melt complex compound. The finished melt is fed by means of a dosage pump 12 to a rotating nozzle 4 in the upper portion of the chamber 1. The amount and evenness of the feed is achieved by the aid of an accurate valveless cylinder dosage pump 12 and a pulse attenuator 14. The temperature of the melt is kept constant and accurately regulated in the feed piping 11 and 13 and in the pump 12 by means of an oil heating mantle 15 of the piping 11 and 13.

The rotating nozzle 4 is closed in structure so that nothing else but melt to be sprayed goes into it. The rotating nozzle 4 preferably is a hollow disc, which when rotating at a rate of 18,000 to 25,000rpm sprays small melt droplets to the spraying area 5 through small nozzle holes in the outer surface of its periphery.

From the nozzle 4 the melt is sprayed to the spraying area of the chamber 1, in which the droplets are kept apart from each other by the aid of inert gas fed into the upper portion of the chamber 1 close to the nozzle 4. The inert gas flow is regulated by means of dividing plates 8 to prevent the agglomeration of the melt droplets.

From the spraying area 5 the droplets or particles fall apart from each other downwards in chamber 1 colliding in the middle portion of the chamber to another gas flow fed from a separate feeder pipe 8. This gas flow is colder than the above-mentioned gas flow and causes a total solidification and at least a partial crystallization in the droplets or particles. When the droplets or particles have come into contact with the last-mentioned gas flow they crystallize in the crystallizing area 6 and get their final physical properties. The inert gas used is removed from the outlet pipe 9 in the lower portion of the chamber and the finished solid carrier particles fall on the conical bottom of the chamber, in the middle of which is the outlet opening 10 of them.

In Fig. 2 there can be seen the rotating disc nozzle 4 according to one embodiment of the invention, to which no gas can get from the surrounding.

The melt is fed into the nozzle through cone 16 so that it fills the hollow space 17 of the disc 4.

In the outer periphery surface of the disc 4 there are the nozzle holes 18, through which the melt is thrown to the spraying area by the aid of centrifugal force.

The diameter of the disc nozzle shown in the figure preferably is 100 to 150mm and it preferably has four nozzle holes, the diameter of which is about 4mm. It preferably rotates with the speed of rotation of about 20,000rpm.

In the following an example is presented for the illustration of the invention.

Example**Preparation of the melt**

In the preparation of the melt  $\text{MgCl}_2$  is first dosed to the reactor and after that the ethanol and the optional internal donor announced in the table I. The reactor is closed and the heating is started. When the temperature of the reactor is  $+120^\circ\text{C}$ , the mixer is started and the increasing of the temperature is continued until  $+130^\circ\text{C}$ . The agitation time of the melt depends on the amount of the  $\text{MgCl}_2$  to be dosed so that 26kg of  $\text{MgCl}_2$  requires an agitation of four hours at  $130^\circ\text{C}$  and 52kg six hours at the same temperature.

**Processing conditions**

As the gas coming to the chamber dried nitrogen is used, which is conducted into two points of the chamber according to figure 1. The best angle of the gas dividing plate in the upper portion of the chamber 1 is  $45^\circ$  with respect to the vertical line so that the gas coming inside the chamber 1 circulates in the same direction as the rotating disc 4.

The speed of rotation of the rotating nozzle is 24,000rpm and it is closed in structure and it has four nozzle holes having the diameter of 4mm. The feeding rate of the melt is 30kg/h for all the carriers of the table.

**The results**

The best processing conditions for the various melt compositions have been presented in Table I.

Table I

Carrier	Feed temperature of the melt $^\circ\text{C}$	$T_1$ $^\circ\text{C}$	$T_2$ $^\circ\text{C}$	$F_1$ kg/h	$F_2$ kg/h
$\text{MgCl}_2$ 3, 0EtOH	130	35	10	500	300
$\text{MgCl}_2$ 3, 5EtOH	120	30	10	500	300
$\text{MgCl}_2$ 4, 0EtOH	115	28	5	500	300
$\text{MgCl}_2$ 4, 5EtOH	110	25	0	500	300
$\text{MgCl}_2$ 3, 5EtOH 0.05 DIPB	115	35	-5	500	300
$\text{MgCl}_2$ 3, 5EtOH 0.05 DEME	110	35	-5	500	300

In Table I EtOH depicts ethanol, DIPB di-isobutyl phthalate and DEME diethylmaleate.  $T_1$  and  $F_1$  depict the corresponding temperature and flow amount of the inert gas fed into the upper portion of the chamber 1 according to figure 1 through pipe 7 and  $T_2$  and  $F_2$  depict the corresponding temperature and flow amount of the other inert gas flow fed into the middle portion of the chamber 1 through pipe 8.

When in the present invention an equipment according to figures 1 and 2 and the above-described conditions were used carrier particles were obtained, the morphology, particle size and particle size distribution of which were retained when they were activated with titanium tetrachloride. The average particle size of the carrier activated with titanium tetrachloride was below  $70\mu\text{m}$ , whereby the cumulative mass portion of the particles of below  $20\mu\text{m}$  was below 10%. The narrowness  $\{(d_{90}-d_{50})/d_{10}\}$  of the whole distribution was below 1.5.

Copolymerization was carried out with the catalyst, whereby triethyl aluminium was used as the cocatalyst. In the polymerization tests about 17kg PP/g was obtained as a typical activity of the catalyst, whereby the bulk density of the polymer was 0.42 and its isotacticity index 98.0.

**Claims**

1. A method for the preparation of solid carrier particles for a polymerization catalyst, in which a melt of a complex composition is provided having the formula (I)



in which ROH represents an aliphatic alcohol, R is a  $\text{C}_1\text{-C}_6$  alkyl, ED represents an electron donor, n is 1 to 6 and m is 0 to 1; the melt provided is fed to a nozzle (4); the melt is sprayed from the nozzle (4) to the spraying area (5) in which it is divided into fine melt droplets and possibly partly solidifies; the melt particles which are possibly

partly solidified are transferred to a cooled crystallization area (6), where they crystallize to solid carrier particles; and the solid carrier particles are recovered, **characterized in that** the melt mentioned is sprayed through a nozzle (4), which is rotated or which has attached to it a member that rotates and throws melt outwards from the rotating center to the spraying area (5).

2. Method according to Claim 1, **characterized in that** the speed of rotation of the rotating nozzle (4) or the member attached to it is about 10,000 to 30,000rpm, preferably 18,000 to 25,000rpm.
3. Method according to Claim 1 or 2, **characterized in that** a hollow disc rotating around its axis is used as the rotating nozzle (4), inside (17) which the melt is led and having in its outer periphery surface holes (18) through which the melt is forced out by the aid of centrifugal force.
4. Method according to Claim 3, **characterized in that** the diameter of the rotating hollow disc (4) is about 100 to 150mm.
5. Method according to Claim 3 or 4, **characterized in that** in the outer periphery surface of the rotating hollow disc (4) there are four nozzle holes (18), the diameter of which preferably is about 4mm.
6. Method according to Claim 3, 4, or 5, **characterized in that** the rotating hollow disc (4) is closed in structure, so that its hollow space (17) is through the inlet opening (16) in contact with the feeder pipe (13) of the melt and through the holes (18) mentioned in contact with the spraying area (5).
7. Method according to any of the preceding Claims, **characterized in that** to the spraying area (5) is conducted (7) inert gas, which is directed close to the nozzle (4) and the temperature of which preferably is about 20 to 40°C and the flowing rate preferably is about 500kg/h.
8. Method according to Claim 7, **characterized in that** the inert gas led to the spraying area (5) is directed by the aid of a dividing plate (8) so that the inert gas mentioned circulates in the same direction as the rotating nozzle (4) or the rotating member attached to it.
9. Method according to any of the preceding Claims, **characterized in that** the feeding rate of the melt to the nozzle is about 10 to 50kg/h and that its feeding temperature preferably is about 100 to 140°C.
10. Method according to any of the preceding Claims, **characterized in that** a vertical chamber (1) is used, in the upper end of which there is the nozzle (4) mentioned, in the upper portion there is a spraying area (5) and in the lower portion there is a crystallization area (6) and in the lower end there is a recovery opening (10) of the solid carrier particles.
11. Method according to any of the preceding Claims, **characterized in that** to the crystallization area (6) or between the spraying area (5) and the crystallizing area there is conducted inert gas through pipe (8).
12. Method according to Claim 11, **characterized in that** the temperature of inert gas led to the crystallization area (6) or between the spraying area (5) and the crystallization area (6) is -50 to +20°C and the flowing rate preferably about 300kg/h.
13. Method according to any of the preceding Claims, **characterized in that** ROH is ethanol, whereby n preferably is 3 to 4.
14. Method according to any of the preceding Claims, **characterized in that** ED is dialkyl phthalate, preferably diisobutyl phthalate, or dialkyl maleate, preferably diethyl maleate.
15. Method according to any of the preceding Claims, **characterized in that** m is about 0.05.
16. Method according to any of the preceding Claims, **characterized in that** non-porous particles are prepared by it, the SPAN figure of which describing the particle size distribution is about 1.1 to 1.6.
17. Method according to any of the preceding Claims, **characterized in that** the recovered solid carrier particles are brought together with a transition metal compound capable of being catalytically activated, such as titanium tetra-

chloride, to provide an active olefin polymerization catalyst.

18. The use of an olefin polymerization catalyst prepared by a method according to Claim 17 together with a cocatalyst and optionally an external donor for the polymerization of olefins.

## Patentansprüche

1. Verfahren zur Herstellung fester Trägerteilchen für einen Polymerisationskatalysator, in welchem eine Schmelze einer komplexen Zusammensetzung der Formel (I)



bereitgestellt wird, worin ROH einen aliphatischen Alkohol darstellt, R ein C<sub>1</sub>-C<sub>6</sub>-Alkyl ist, ED einen Elektronendonator darstellt, n 1 bis 6 ist und m 0 bis 1 ist; die bereitgestellte Schmelze einer Düse (4) zugeführt wird; die Schmelze aus der Düse (4) in den Sprühhbereich (5) versprüht wird, in dem sie in feine Schmelztröpfchen zerteilt wird und sich gegebenenfalls teilweise verfestigt; die Schmelzteilchen, die sich möglicherweise teilweise verfestigt haben, in einen gekühlten Kristallisationsbereich (6) überführt werden, in dem sie zu festen Trägerteilchen kristallisieren; und die festen Trägerteilchen gewonnen werden, dadurch gekennzeichnet, daß die erwähnte Schmelze durch eine Düse (4) versprüht wird, die sich dreht oder die ein an ihr befestigtes Element aufweist, das sich dreht und Schmelze von dem Drehzentrum in den Sprühhbereich (5) nach außen hin auswirft.

2. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß die Drehgeschwindigkeit der sich drehenden Düse (4) oder des an ihr befestigten Elements etwa 10 000 bis 30 000 U/min, vorzugsweise 18 000 bis 25 000 U/min beträgt.

3. Verfahren gemäß den Ansprüchen 1 oder 2, dadurch gekennzeichnet, daß eine hohle Scheibe, die sich um ihre Achse dreht, als sich drehende Düse (4) verwendet wird, in deren Inneres (17) die Schmelze eingeführt wird und die in ihren Außenumfang Oberflächenlöcher (18) aufweist, durch welche die Schmelze mit Hilfe der Zentrifugalkraft herausgepreßt wird.

4. Verfahren gemäß Anspruch 3, dadurch gekennzeichnet, daß der Durchmesser der sich drehenden, hohlen Scheibe (4) etwa 100 bis 150 mm beträgt.

5. Verfahren gemäß den Ansprüchen 3 oder 4, dadurch gekennzeichnet, daß in der Außenumfangs-Oberfläche der sich drehenden, hohlen Scheibe (4) vier Düsenlöcher (18) vorliegen, deren Durchmesser vorzugsweise etwa 4 mm beträgt.

6. Verfahren gemäß den Ansprüchen 3, 4 oder 5, dadurch gekennzeichnet, daß die sich drehende, hohle Scheibe (4) eine geschlossene Struktur aufweist, so daß ihr Hohlraum (17) durch die Einlaßöffnung (16) mit dem Zuführungsrohr (13) der Schmelze in Kontakt steht und durch die erwähnten Löcher (18) mit dem Sprühhbereich (5) in Kontakt steht.

7. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß zu dem Sprühhbereich (5) ein inertes Gas (7) geleitet wird, welches in die Nähe der Düse (4) gerichtet wird und dessen Temperatur vorzugsweise etwa 20 bis 40 °C beträgt und dessen Fließgeschwindigkeit vorzugsweise etwa 500 kg/h ausmacht.

8. Verfahren gemäß Anspruch 7, dadurch gekennzeichnet, daß das inerte Gas, das zu dem Sprühhbereich (5) geleitet wird, mit Hilfe einer Teilplatte (8) so ausgerichtet wird, daß das erwähnte inerte Gas in der gleichen Richtung zirkuliert wie die sich drehende Düse (4) oder das an ihre befestigte sich drehende Element.

9. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Zugabegeschwindigkeit der Schmelze zu der Düse etwa 10 bis 50 kg/h beträgt, und die Zugabetemperatur vorzugsweise etwa 100 bis 140 °C beträgt.

10. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß eine vertikale Kam-



mer (1) verwendet wird, wobei sich in dem oberen Ende derselben die erwähnte Düse (4) befindet, in dem oberen Teil ein Sprühhbereich (5) vorliegt und in dem unteren Teil ein Kristallisationsbereich (6) vorliegt und in dem unteren Ende eine Öffnung (10) zur Gewinnung der festen Trägereilchen vorliegt.

11. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß zu dem Kristallisationsbereich (6) oder zwischen dem Sprühhbereich (5) und dem Kristallisationsbereich (6) ein inertes Gas durch das Rohr (8) geleitet wird.
12. Verfahren gemäß Anspruch 11, dadurch gekennzeichnet, daß die Temperatur des inertes Gases, das zu dem Kristallisationsbereich (6) oder zwischen den Sprühhbereich (5) und den Kristallisationsbereich (6) geführt wird, eine Temperatur von -50 bis +20 °C aufweist, und die Fließgeschwindigkeit vorzugsweise etwa 300 kg/h beträgt.
13. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß ROH Ethanol ist, wobei n vorzugsweise 3 bis 4 ist.
14. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß ED Dialkylphthalat, vorzugsweise Diisobutylphthalat, oder Dialkylmaleat, vorzugsweise Diethylmaleat ist.
15. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß m etwa 0,05 ist.
16. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß durch dasselbe nichtporöse Teilchen hergestellt werden, deren SPAN-Zahl, die die Teilchengrößenverteilung beschreibt, etwa 1,1 bis 1,6 beträgt.
17. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die gewonnenen festen Trägereilchen zusammengebracht werden mit einer Übergangsmetall-Verbindung, wie Titan-tetrachlorid, die zur katalytischen Aktivierung befähigt ist, um einen aktiven Olefin-Polymerisationskatalysator bereitzustellen.
18. Verwendung eines Olefin-Polymerisationskatalysators, der durch ein Verfahren gemäß Anspruch 17 hergestellt wird, zusammen mit einem Cokatalysator und gegebenenfalls einem externen Donor für die Polymerisation von Olefinen.

## Revendications

1. Un procédé de préparation de particules solides de support pour un catalyseur de polymérisation, dans lequel est prévu un produit fondu d'une composition complexe présentant la formule (I)



dans lequel ROH représente un alcool aliphatique, R est un alkyle en C<sub>1</sub> à C<sub>6</sub>, ED représente un donneur d'électrons, n est de 1 à 6 et m est de 0 à 1 ; le produit fondu prévu est amené à une buse (4) ; le produit fondu est pulvérisé depuis la buse (4) sur la zone de pulvérisation (5) dans laquelle il se divise en fines gouttelettes de produit fondu et se solidifie éventuellement en partie ; les particules de produit fondu qui sont éventuellement en partie solidifiées sont transférées vers une zone de cristallisation refroidie (6) où elles cristallisent en particules solides de support ; et les particules solides de support sont récupérées, **caractérisé en ce que** le produit fondu mentionné est pulvérisé à travers une buse (4), laquelle est entraînée en rotation ou présente, fixé à celle-ci, un élément qui tourne et projette le produit fondu vers l'extérieur depuis le centre de rotation jusqu'à la zone de pulvérisation (5).

2. Procédé selon la revendication 1, **caractérisé en ce que** la vitesse de rotation de la buse rotative (4) ou de l'élément fixé à celle-ci est d'environ 10 000 à 30 000 tpm, de préférence de 18 000 à 25 000 tpm.
3. Procédé selon la revendication 1 ou 2, **caractérisé en ce qu'un** disque creux tournant autour de son axe est utilisé en tant que buse rotative (4), à l'intérieur (17) de laquelle le produit fondu est amené et qui présente, dans sa surface périphérique externe, des trous (18) à travers lesquels le produit fondu est amené à force à sortir à l'aide

de la force centrifuge.

4. Procédé selon la revendication 3, **caractérisé en ce que** le diamètre du disque creux rotatif (4) est d'environ 100 à 150 mn.
5. Procédé selon la revendication 3 ou 4, **caractérisé en ce que**, dans la surface périphérique externe du disque creux rotatif (4) se trouve quatre trous de buse (18) dont le diamètre est de préférence d'environ 4 mm.
6. Procédé selon la revendication 3, 4 ou 5, **caractérisé en ce que** le disque creux rotatif (4) est de structure fermée, de sorte que son espace creux (17) est, par l'intermédiaire de l'ouverture d'entrée (16), en contact avec la canalisation d'amenée (13) du produit fondu et, par l'intermédiaire des trous (18) mentionnés, en contact avec la zone de pulvérisation (5).
7. Procédé selon une quelconque des revendications précédentes, **caractérisé en ce qu'un** gaz inerte (7) est amené à la zone de pulvérisation (5) en étant dirigé près de la buse (4), sa température est de préférence d'environ 20 à 40°C et sa vitesse d'écoulement est de préférence d'environ 500 kg/h.
8. Procédé selon la revendication 7, **caractérisé en ce que** le gaz inerte amené à la zone de pulvérisation (5) est dirigé à l'aide d'une plaque diviseuse (8) de sorte que le gaz inerte mentionné circule dans la même direction que la buse rotative (4) ou que l'élément rotatif qui lui est fixé.
9. Procédé selon une quelconque des revendications précédentes, **caractérisé en ce que** la vitesse d'amenée du produit fondu vers la buse est d'environ 10 à 50 kg/h et en ce que sa température d'amenée est de préférence d'environ 100 à 140°C.
10. Procédé selon une quelconque des revendications précédentes, **caractérisé en ce qu'on** utilise une chambre verticale (1) à l'extrémité supérieure de laquelle se trouve la buse (4) mentionnée, à la partie supérieure se trouve une zone de pulvérisation (5), à la partie inférieure se trouve une zone de cristallisation (6) et à l'extrémité inférieure se trouve une ouverture de récupération (10) des particules solides de support.
11. Procédé selon une quelconque des revendications précédentes, **caractérisé en ce qu'un** gaz inerte est amené par l'intermédiaire d'un conduit (8) à la zone de cristallisation (6) ou entre la zone de pulvérisation (5) et la zone de cristallisation.
12. Procédé selon la revendication 11, **caractérisé en ce que** la température du gaz inerte amené à la zone de cristallisation (6) ou entre la zone de pulvérisation (5) et la zone de cristallisation (6) est de -50 à + 20°C, et en ce que la vitesse d'écoulement est de préférence d'environ 300 kg/h.
13. Procédé selon une quelconque des revendications précédentes, **caractérisé en ce que** ROH est l'éthanol, de sorte que n est de préférence de 3 à 4.
14. Procédé selon une quelconque des revendications précédentes, **caractérisé en ce que** ED est du phtalate de dialkyle, de préférence du phtalate de di-isobutyle, ou du maléate de di-alkyle, de préférence du maléate de di-éthyle.
15. Procédé selon une quelconque des revendications précédentes, **caractérisé en ce que** m est d'environ 0,05.
16. Procédé selon une quelconque des revendications précédentes, **caractérisé en ce que** des particules non poreuses sont préparées par ce dernier, le chiffre SPAN de celles-ci décrivant la répartition de granulométrie est d'environ 1,1 à 1,6.
17. Procédé selon une quelconque des revendications précédentes, **caractérisé en ce que** les particules solides de support récupérées sont amenées en même temps qu'un composé d'un métal de transition capable d'être activé de manière catalytique, tel que du tétrachlorure de titane, pour créer un catalyseur actif de polymérisation des oléfines.
18. L'utilisation d'un catalyseur de polymérisation des oléfines préparées par un procédé selon la revendication 17 en même qu'un co-catalyseur et éventuellement un donneur externe pour la polymérisation des oléfines.

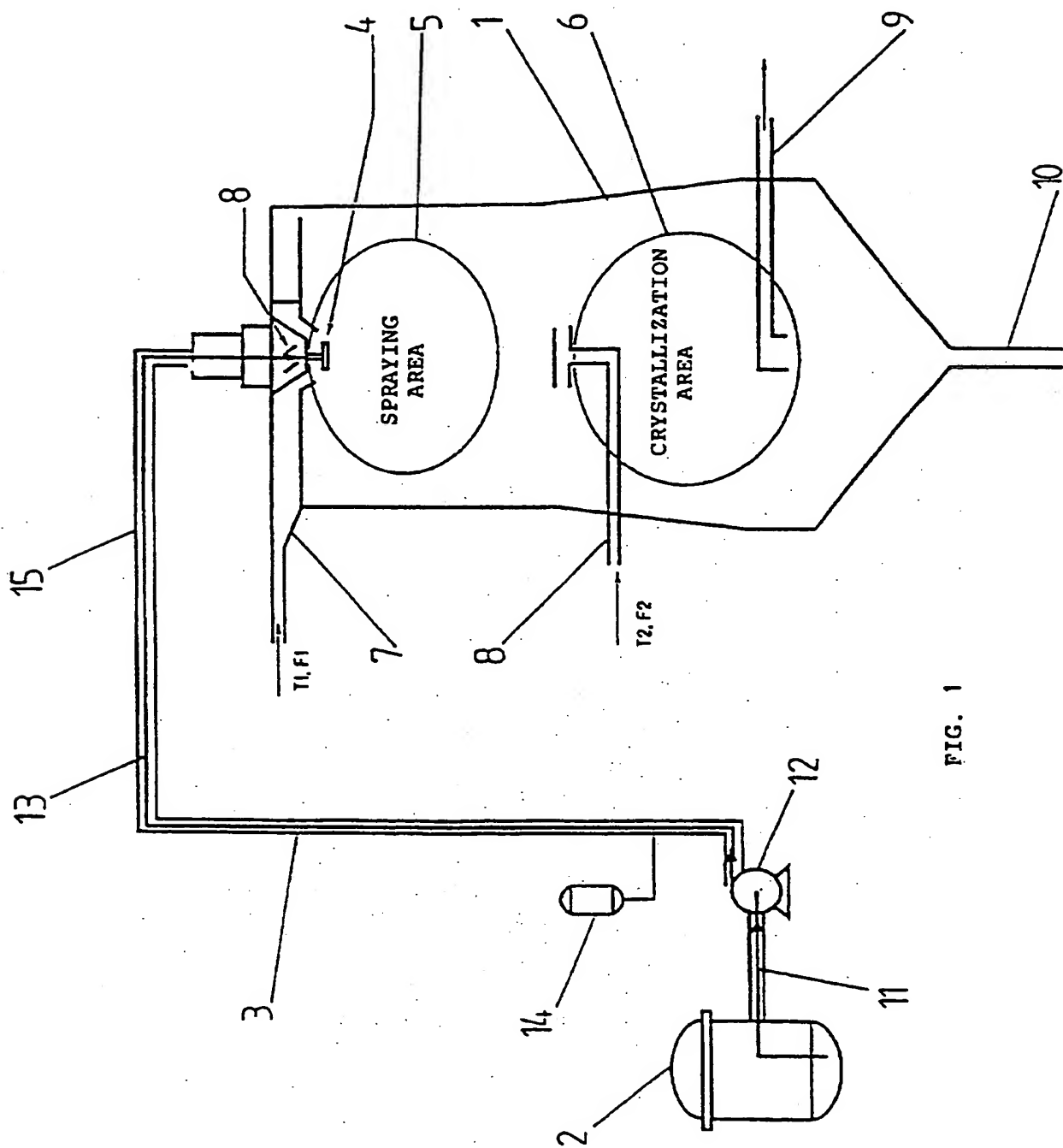


FIG. 1

**THIS PAGE BLANK (USPTO)**

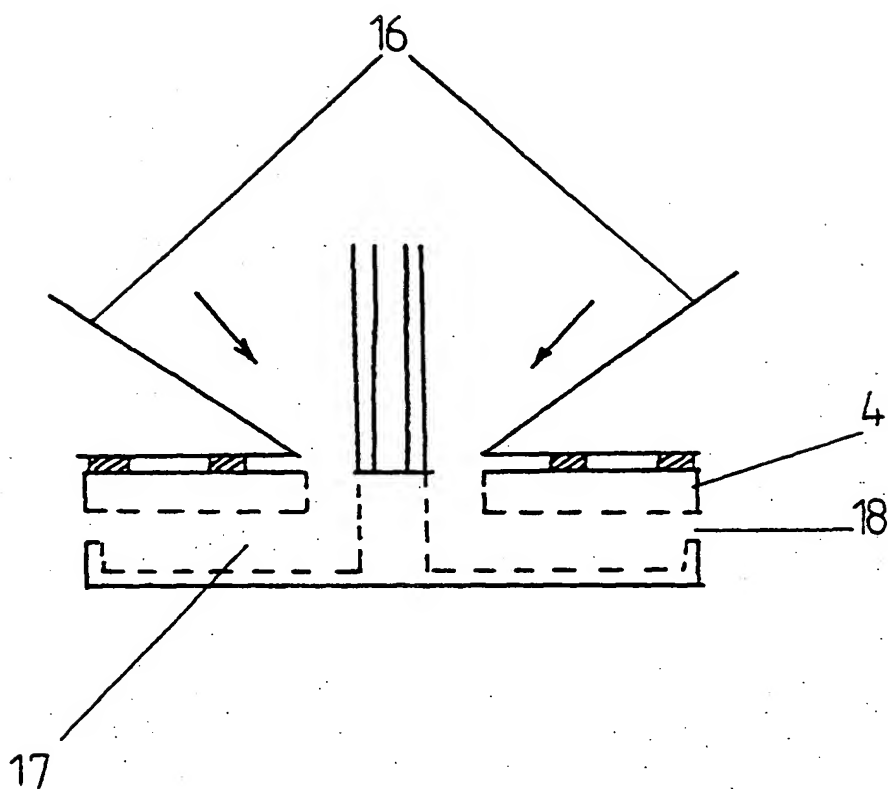


FIG. 2

**THIS PAGE BLANK (USPTO)**